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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C08J 3/24, C09D 167/00, 133/06

A1

(11) International Publication Number: WO 98/00456

(43) International Publication Date: 8 January 1998 (08.01.98)

(21) International Application Number: PCT/EP97/03219

(22) International Filing Date: 20 June 1997 (20.06.97)

(30) Priority Data:
96810438.0 2 July 1996 (02.07.96) EP

(34) Countries for which the regional or international application was filed: DE et al.

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
With amended claims.

(54) Title: PROCESS FOR CURING A POLYMERIZABLE COMPOSITION

(57) Abstract

By means of a curing process combining thermal and UV curing, it is possible, using compositions comprising (A) a coating system based on a polyacrylate polyol or polyester polyol with melamine, or a polyacrylate polyol and/or polyester polyol with a blocked or unblocked polyisocyanate, or a carboxyl-, anhydride- or amino-functional polyester and/or polyacrylate with an epoxy-functional polyester or polyacrylate, (B) an OH-, NH_2-, COOH-, epoxy- or NCO-functional resin containing, in addition, at least one ethylenically unsaturated double bond, which is separated from the functional group by a spacer group, and (C) at least one photoinitiator, to obtain coatings having good surface properties.

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PROCESS FOR CURING A POLYMERIZABLE COMPOSITION

The invention relates to a process for the curing of surface coatings, whereby the surface hardness of the cured surface coating is increased by means of irradiation with UV light, and to a polymerisable composition.

In US Patent 4 121 985 the resistance of thermoplastic polyurethane surfaces to solvents and abrasion is improved by treatment of the surface with a mixture of solvent and photo-initiator and by subsequent irradiation with UV light. Derwent No. 94-252879/31 (JP-A Hei 6 184267) describes a polyurethane resin obtained by reacting polyol mixtures, containing chlorinated polyols and polyols having COOH groups, with polyisocyanates and unsaturated monohydroxy compounds and, where appropriate, a photoinitiator. DE-A 42 37 695 claims surface-coating compositions that contain functionalised resins having α,β-unsaturated groups and that are cured thermally. Derwent No. 87-331357 (JP-A Sho 62 236867) describes a curing process combining thermal and photochemical curing. Derwent No. 85-188037 (JP-A Sho 60 118271) discloses a combined heat- and UV-curable composition. EP-A 600 262 claims photoresist compositions having heat- and UV-curable components. In DE-A 33 32 004 and EP-A 247 563 there are prepared UV-curable surface-coating systems that comprise epoxide/amine- or polyol/isocyanate-based resins.

In the art there is a need for resins for coatings and surface coatings that exhibit good properties especially in respect of the durability of the cured surface.

It has now been found, surprisingly, that coatings having very good surface properties can be obtained by means of a process for the curing of a polymerisable composition comprising

(A) a coating system based on

(I) a polyacrylate polyol and/or polyester polyol with melamine or

(II) a polyacrylate polyol and/or polyester polyol with a blocked or unblocked polyisocyanate or

(III) a carboxyl-, anhydride- or amino-functional polyester and/or polyacrylate with an epoxy-functional polyester or polyacrylate, or

(IV) a mixture of (I), (II), (III) and/or (IV),

(B) an OH-, NH_2-, COOH-, epoxy- or NCO-functional resin containing, in addition, at least one ethylenically unsaturated double bond, it being necessary for a spacer group of at least 4 linearly linked atoms to be present between the double bond and the functional group,

wherein components (A) and (B) do not contain halogen, and

(C) at least one photoinitiator,

by thermal treatment and, for the purpose of improving the surface properties, subsequent photochemical treatment with light of a wavelength from 200 to 600 nm.

The invention relates also to a composition comprising

(A) a coating system based on

(I) a polyacrylate polyol and/or polyester polyol with melamine or

(II) a polyacrylate polyol and/or polyester polyol with a blocked or unblocked polyisocyanate or

(III) a carboxyl-, anhydride- or amino-functional polyester and/or polyacrylate with an epoxy-functional polyester or polyacrylate, or

(IV) a mixture of (I), (II), (III) and/or (IV),

(B) an OH-, NH_2-, COOH-, epoxy- or NCO-functional resin containing, in addition, at least one ethylenically unsaturated double bond, it being necessary for a spacer group of at least 4 linearly linked atoms to be present between the double bond and the functional group,

wherein components (A) and (B) do not contain halogen, and

(C) at least one photoinitiator.

Constituents of component (A) are, for example, surface-coating or coating-system constituents that are customary in the art. In the context of the present invention, component (A) represents a surface coating or a coating.

Constituents of component (A) are, for example, polymers that are derived from α,β-unsaturated acids or from derivatives thereof. Examples thereof are polyacrylates and polymethacrylates, polymethylmethacrylates impact-resistant modified with butyl acrylate, polyacrylamides and polyacrylonitriles. Also of interest are, for example, silicone acrylates. Further constituents of component (A) may be polyurethanes that are derived on the one hand from polyethers, polyesters and polyacrylates having free hydroxy groups and on the

other hand from aliphatic or aromatic polyisocyanates, and precursors thereof. The constituents of component (A) also include, for example, cross-linkable acrylic resins that are derived from substituted acrylic acid esters, for example epoxy acrylates, urethane acrylates or polyester acrylates. Furthermore, alkyd resins, polyester resins and acrylate resins, and modifications thereof, that are cross-linked with melamine resins, urea resins, isocyanates, isocyanurates, polyisocyanates, polyisocyanurates or epoxy resins may be a constituent of component (A).

Component (A) is, for example, generally a film-forming binder based on a thermoplastic or thermocurable resin, predominantly on a thermocurable resin. Examples thereof are alkyd, acrylic, polyester, phenol, melamine, epoxy and polyurethane resins and mixtures thereof. Examples thereof are described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A18, pp. 368-426, VCH, Weinheim 1991.

Component (A) may be a cold-curable or hot-curable binder, with the addition of a curing catalyst possibly being advantageous. Suitable catalysts that accelerate the full cure of the binder are described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A18, p. 469, VCH Verlagsgesellschaft, Weinheim 1991.

Examples of coatings (A) with specific binders are:

1. surface coatings based on cold- or hot-cross-linkable alkyd, acrylate, polyester, epoxy or melamine resins or mixtures of such resins, where appropriate with the addition of a curing catalyst;
2. two-component polyurethane surface coatings based on hydroxy-group-containing acrylate, polyester or polyether resins and aliphatic or aromatic isocyanates, isocyanurates or polyisocyanates;
3. one-component polyurethane surface coatings based on blocked isocyanates, isocyanurates or polyisocyanates that are de-blocked during stoving; if desired, the addition of melamine resins is also possible;
4. one-component polyurethane surface coatings based on aliphatic or aromatic urethanes or polyurethanes and hydroxy-group-containing acrylate, polyester or polyether resins;
5. one-component polyurethane surface coatings based on aliphatic or aromatic urethane acrylates or polyurethane acrylates having free amine groups in the urethane structure and

melamine resins or polyether resins, where appropriate with the addition of a curing catalyst;

6. two-component surface coatings based on (poly)ketimines and aliphatic or aromatic isocyanates, isocyanurates or polyisocyanates;

7. two-component surface coatings based on (poly)ketimines and an unsaturated acrylate resin or a polyacetoacetate resin or a methacrylamidoglycolate methyl ester;

8. two-component surface coatings based on carboxyl-group- or amino-group-containing polyacrylates and polyepoxides;

9. two-component surface coatings based on anhydride-group-containing acrylate resins and a polyhydroxy or polyamino component;

10. two-component surface coatings based on acrylate-containing anhydrides and polyepoxides;

11. two-component surface coatings based on (poly)oxazolines and anhydride-group-containing acrylate resins or unsaturated acrylate resins or aliphatic or aromatic isocyanates, isocyanurates or polyisocyanates;

12. two-component surface coatings based on unsaturated polyacrylates and polymalonates;

13. thermoplastic polyacrylate surface coatings based on thermoplastic acrylate resins or extrinsically cross-linking acrylate resins in combination with etherified melamine resins;

14. surface-coating systems based on siloxane-modified acrylate resins.

Blocked isocyanates as may be used in component (A) are described, for example, in Organischer Metallschutz: Entwicklung und Anwendung von Beschichtungsstoffen, pp. 159-160, Vincentz Verlag, Hannover (1993). Such compounds are those wherein the highly reactive NCO group is "blocked" by reaction with specific radicals, for example, primary alcohols, phenol, ethyl acetoacetate, ε-caprolactam, phthalimide, imidazole, oxime and amine. The blocked isocyanate is stable in liquid systems and also in the presence of hydroxy groups. On heating, the blocking agents are removed again and the NCO group is freed.

1-component (1C) and 2-component (2C) systems are described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A18, Paints and Coatings, pp. 404-407, VCH Verlagsgesellschaft mbH, Weinheim (1991).

It is possible to optimise the composition by specially adapting the formulation, for example by varying the binder/cross-linker ratio. The person skilled in the art of surface-coating technology will be familiar with such measures.

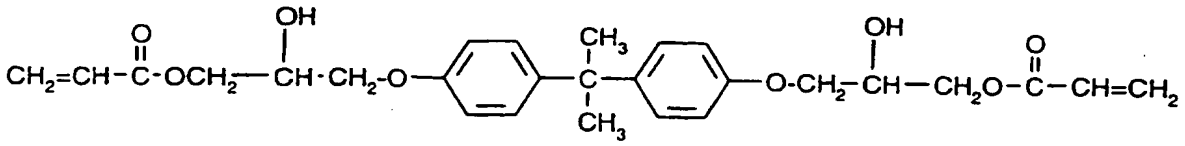
In the curing process according to the invention the composition is preferably a composition based on acrylate/melamine, 2-component polyurethane, 1-component polyurethane, 2-component epoxy or 1-component epoxy/carboxy. Mixtures of those systems are also possible, for example the addition of melamine to 1-component polyurethanes.

Component (A) is preferably a binder based on a polyacrylate with melamine.
Preference is given also to a system based on a polyacrylate polyol and/or polyester polyol with an unblocked polyisocyanate.

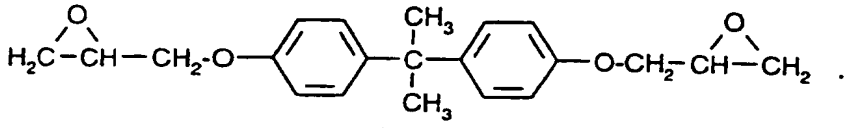
Component (B) consists essentially of monomeric and/or oligomeric compounds having ethylenically unsaturated bonds (pre-polymers) that, in addition, contain at least one or more OH, NH_2, COOH, epoxy or NCO groups capable of reacting with the binder and/or cross-linker of component (A). After application and thermal curing, the ethylenically unsaturated bonds are converted into a cross-linked, high-molecular-weight form by means of UV radiation. Examples of component (B) are described, for example, in the publication mentioned hereinbefore, Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A18, pp. 451-453, or by S. Urano, K. Aoki, N. Tsuboniva and R. Mizuguchi in Progress in Organic Coatings, 20 (1992), 471-486, or by H. Terashima and O. Isozaki in JOCCA 1992 (6), 222.
(B) may be, for example, an OH-group-containing, unsaturated acrylate, for example hydroxyethyl acrylate, hydroxybutyl acrylate or a glycidyl acrylate.
Component (B) may have any desired structure (for example it may contain units of polyester, polyacrylate, polyether, etc.) provided that it includes an ethylenically unsaturated double bond and also, in addition, free OH, COOH, NH_2, epoxy or NCO groups.

(B) may also be obtained, for example, by reacting an epoxy-functional oligomer with acrylic acid or methacrylic acid.

A typical example of an OH-functional oligomer having vinylic double bonds is



obtained by reaction of $CH_2=CHCOOH$ with



A further possible method of preparing component (B) is, for example, the reaction of an oligomer that contains only one epoxy group and has a free OH group in another position in the molecule.

Also suitable as component (B) are, for example, siloxane-group-containing polymers that contain free OH groups and, in addition, free double bonds. Those polymers can be obtained, for example, by reacting an epoxy-functional polysiloxane with acrylic acid or methacrylic acid or derivatives thereof, for example $CH_2=CHCOO\text{-}CH_2CH(OH)CH_2O\text{-}(CH_2)_m\text{-}[Si(CH_3)_2\text{-}O]_n\text{-}Si(CH_3)_2\text{-}(CH_2)_m\text{-}OCH_2CH(OH)CH_2OC(O)CH=CH_2$. Such products are available commercially.

Suitable spacer groups of at least 4 linearly linked atoms positioned between the double bond and the functional group in component (B) are, for example, the following structures: $-(CH_2)_y-$, wherein $y \geq 4$, or $-C(=O)-O-(CH_2)_y-$, wherein $y \geq 2$, or $-C(=O)-O-(C_xH_{2x})_y-$, wherein x = from 1 to 3 and $y \geq 2$. Preference is given to $-C(=O)-O-(CH_2)_y-$. The number of spacer atoms is at least 4, for example from 4 to 16, 6-16, preferably from 4 to 12.

The compositions contain, for example, from 1 to 50 %, e.g. from 5 to 30 %, especially from 10 to 25 %, component (B), based on 100 parts of component (A).

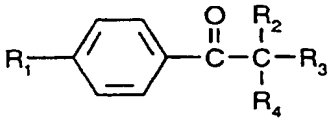
According to the invention there may be used as photoinitiator (C) any known compound that is capable of initiating radical polymerisation when irradiated with light.

Examples thereof are:

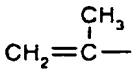
benzophenone, benzophenone derivatives, acetophenone, acetophenone derivatives, for example 1-hydroxy-cyclohexyl-phenyl ketone, 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one or 2-hydroxy-2-methyl-1-phenyl-propanone, dialkoxyacetophenones, α-hydroxy- or α-amino-acetophenones, for example (4-morpholino-benzoyl)-1-benzyl-1-dimethylamino-propane or (4-methylthiobenzoyl)-1-methyl-1-morpholino-ethane, 4-aroyl-1,3-dioxolanes, benzoin alkyl ethers and benzil ketals, for example 2,2-dimethoxy-1,2-diphenyl-ethan-1-one, monoacylphosphine oxides, for example 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide, bisacylphosphine oxides, for example bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphine oxide, bis(2,4,6-trimethylbenzoyl)-(2-methylprop-1-yl)-phosphine oxide, bis(2,4,6-trimethylbenzoyl)phenyl-phosphine oxide and trisacylphosphine oxides.

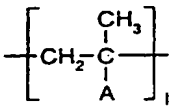
In certain cases it may be advantageous to use mixtures of two or more photoinitiators, for example mixtures of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphine oxide or bis(2,4,6-trimethylbenzoyl)-phenyl-phosphine oxide with 1-hydroxy-cyclohexyl-phenyl ketone or hydroxy-2-methyl-1-phenyl-propanone or 2-methoxy-1-phenyl-ethane-1,2-dione.

Component (C) is preferably a compound of formula I

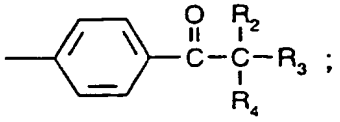


(I) wherein

R_1 is hydrogen, C_1-C_{18}alkyl, C_1-C_{18}alkoxy, $-OCH_2CH_2-OR_5$, a group 

or a group  wherein

l is an integer from 2 to 10 and

A is a radical  ;

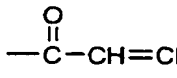
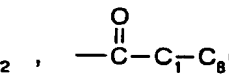
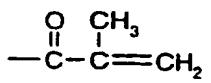
R_2 and R_3 are each independently of the other hydrogen, C_1-C_6alkyl, phenyl, C_1-C_{16}alkoxy, $OSiR_6R_7R_8$ or $-O(CH_2CH_2O)_q$-C_1-C_{16}alkyl wherein

q is an integer from 1 to 20, or

R_2 and R_3, together with the carbon atom to which they are bonded, form a cyclohexyl ring;

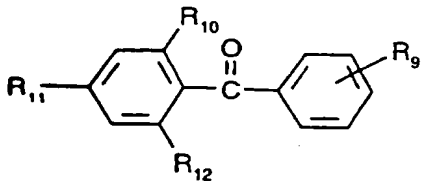
R_4 is hydroxy, C_1-C_{16}alkoxy or $-O(CH_2CH_2O)_q$-C_1-C_{16}alkyl;

with the proviso that R_2, R_3 and R_4 are not all simultaneously C_1-C_{16}alkoxy or $-O(CH_2CH_2O)_q$-C_1-C_{16}alkyl;

R_5 is hydrogen, C_1-C_8alkyl,  ,  or  ;

R_6, R_7 and R_8 are each independently of the others C_1-C_4alkyl or phenyl;

or a compound of formula (Ia)

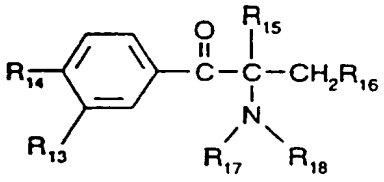


(Ia) wherein

R_9, R_{10}, R_{11} and R_{12} are each independently of the others hydrogen, methyl, phenyl, methoxy, -COOH, unsubstituted or C_1-C_4alkyl-substituted phenyl, or a group $-OCH_2CH_2OR_5$ or $-SCH_2CH_2OR_5$ wherein

R_5 is as defined for formula I;

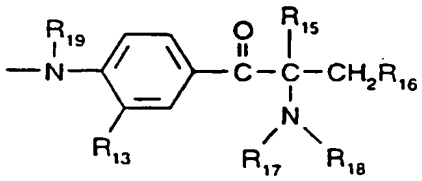
or a compound of formula (Ib)



(Ib) wherein

R_{13} is hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4alkylthio, halogen or a group $N(R_{17})_2$;

R_{14} has one of the meanings indicated for R_{13} or is the group

 , in which case the radical R_{13} from formula Ib and the radical R_{13} from this group are together a direct bond and the other radicals are as defined below;

R_{15} is C_1-C_8alkyl;

R_{16} is hydrogen, -CH=CHR_{20}, or phenyl that is unsubstituted or mono- to tri-substituted by C_1-C_{12}alkyl, C_1-C_4alkoxy or by halogen; or

R_{15} and R_{16}, together with the carbon atom to which they are bonded, form a cyclohexyl ring;

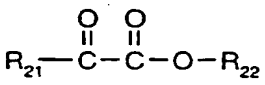
R_{17} and R_{18} are each independently of the other C_1-C_4alkyl or

R_{17} and R_{18}, together with the nitrogen atom to which they are bonded, form a five- or six-membered, saturated or unsaturated ring, which may be interrupted by -O-, -NH- or by -N(CH_3)-,

R_{19} is hydrogen or C_1-C_{12}alkyl; and

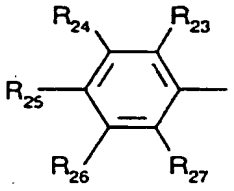
R_{20} is hydrogen or C_1-C_4-alkyl;

or a compound of formula II



(II) wherein

R_{21} is naphthyl, anthracyl, an O- or S-containing, 5- or 6-membered heterocyclic ring or a

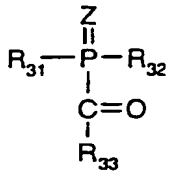
group  ;

R_{22} is C_1-C_{12}alkyl, cyclohexyl, cyclopentyl, C_2-C_{12}alkenyl, phenyl-C_1-C_4alkyl; phenyl, biphenyl or naphthyl each of which is unsubstituted or mono- to tetra-substituted by C_1-C_4alkyl and/or by C_1-C_4alkoxy; C_2-C_{18}alkyl interrupted one or more times by -O-; or Si(R_{28})(R_{29})(R_{30});

R_{23}, R_{24}, R_{25}, R_{26} and R_{27} are each independently of the others hydrogen, C_1-C_8alkyl, C_1-C_8alkoxy, C_1-C_8alkylthio, phenyloxy, phenylthio, phenyl that is unsubstituted or mono- to tetra-substituted by C_1-C_4alkyl and/or by C_1-C_4alkoxy, phenyl-C_1-C_4alkyl, halogen or NO_2;

R_{28}, R_{29} and R_{30} are each independently of the others C_1-C_8alkyl, cyclohexyl, cyclopentyl, phenyl or C_1-C_8alkoxy;

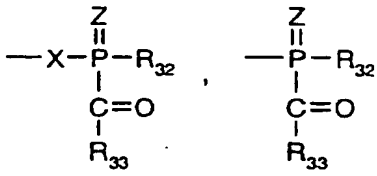
or a compound of formula III



(III) wherein

Z is S or O;

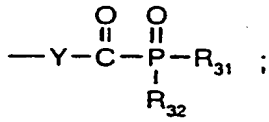
R_{31} and R_{32} are each independently of the other C_1-C_{18}alkyl, C_2-C_{18}alkyl interrupted one or more times by -O-, phenyl-substituted C_1-C_4alkyl, C_2-C_4alkenyl; phenyl, naphthyl or biphenyl each of which is unsubstituted or mono- to penta-substituted by halogen, hydroxy, C_1-C_8alkyl and/or by C_1-C_8alkoxy; C_5-C_{12}cycloalkyl, an O-, S- or N-containing, 5- or 6-membered heterocyclic ring, or a group COR_{33}, or

R_{31} is a radical  , OH, OR_{34}, $O^-NH_4^+$ or $O^-[M^{n+}]_{1/n}$ wherein

n is an integer from 1 to 3 and

M is an n-valent metal ion, or

R_{31} and R_{32} together are C_4-C_7alkylene and form a ring together with the P atom to which they are bonded;

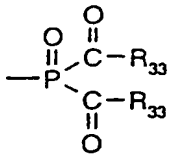
R_{33} is C_1-C_{18}alkyl, C_3-C_{12}cycloalkyl, C_2-C_{18}alkenyl; phenyl, naphthyl or biphenyl each of which is unsubstituted or mono- to tetra-substituted by C_1-C_8alkyl, C_1-C_8alkoxy, C_1-C_8alkylthio and/or by halogen; an O-, S- or N-containing, 5- or 6-membered heterocyclic ring, or a group  ;

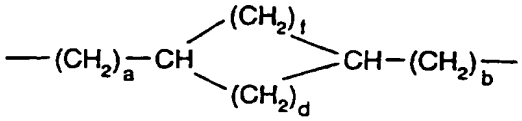
R_{34} is C_1-C_8alkyl, phenyl, naphthyl, C_1-C_8alkylphenyl or C_1-C_4alkylnaphthyl;

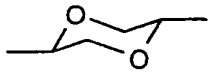
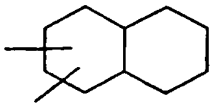
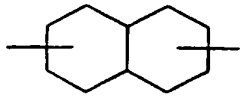
Y is phenylene, C_1-C_{12}alkylene or C_5-C_6cycloalkylene;

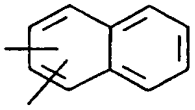
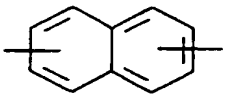
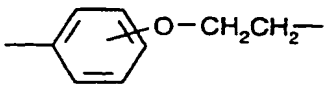
X is C_1-C_{18}alkylene, C_2-C_{18}alkylene interrupted one or more times by -O-, -S-, -NR_{35}-, $P(O)R_{36}$- or by -SO_2-, or C_1-C_6alkylene substituted by Cl, F, C_1-C_4alkoxy, $COOR_{37}$, phenyl, phenyl-C_1-C_4alkyl, naphthyl-C_1-C_4alkyl, C_1-C_4alkylphenyl, C_1-C_4alkylnaphthyl, phenyl-C_1-C_4alkoxy, naphthyl-C_1-C_4alkoxy and/or by CN, or

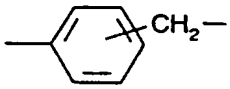
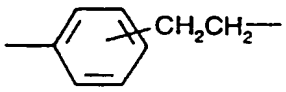
X is C_1-C_8alkylene substituted by one or two radicals of formula A


(A), or

X is a group of formula A_1-A_9  (A_1),

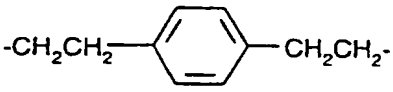
 (A_2),  (A_3),  (A_4),

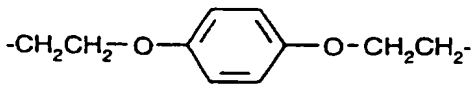
 (A_5),  (A_6),  (A_7),

 (A_8),  (A_9) wherein

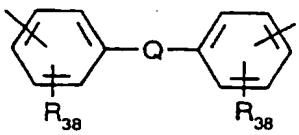
a and b are each independently of the other 0 or 1, and the sum of d and f is an integer from 3 to 8, with the proviso that neither d nor f is 0, or

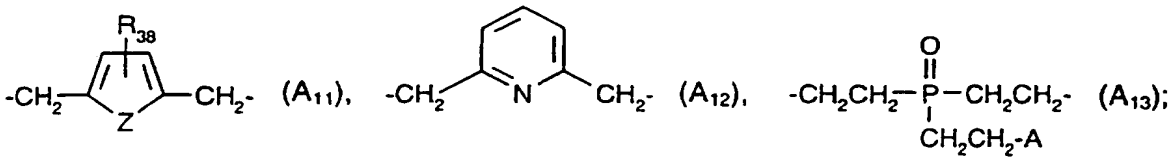
X is a group $-CH_2-CH=CH-CH_2-$ or  , or

X is phenylene, xylylene,  or

 each of which is unsubstituted or mono- to tri-substituted by Cl, F, C_1-C_4alkyl and/or by C_1-C_4alkoxy, or

X is phenylene that is substituted by one or two groups (A) and that, in addition, may be mono- to tri-substituted by Cl, F, C_1-C_4alkyl and/or by C_1-C_4alkoxy, or

X is a group of formula A_{10}-A_{13}  (A_{10}),



Q is a single bond, $CR_{39}R_{40}$, -O-, -S-, $-NR_{35}$-, $-SO_2$-, $-(CH_2)_p$- or -CH=CH-;

p is an integer from 2 to 12;

Z is O or S;

R_{35} is hydrogen, C_1-C_{12}alkyl or phenyl;

R_{36} is C_1-C_4alkyl or phenyl; and

R_{37} is C_1-C_{12}alkyl, C_2-C_{18}alkyl interrupted one or more times by -O-, benzyl, phenyl, cyclopentyl or cyclohexyl;

R_{38} is hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy or halogen;

R_{39} is hydrogen, methyl or ethyl; and

R_{40} is hydrogen or C_1-C_4alkyl;

or component (C) is a mixture of a compound of formula I, Ia, Ib or II with a compound of formula III.

C_1-C_{20}Alkyl is linear or branched and is, for example, C_1-C_{18}-, C_1-C_{12}-, C_1-C_8-, C_1-C_6- or C_1-C_4-alkyl. Examples are methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, hexyl, heptyl, 2,4,4-trimethyl-pentyl, 2-ethylhexyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, heptadecyl, octadecyl and icosyl. C_1-C_{18}Alkyl, C_1-C_{12}alkyl, C_1-C_8alkyl and C_1-C_4alkyl are as defined hereinbefore up to the appropriate number of carbon atoms.

C_2-C_{18}Alkyl interrupted one or more times by -O- or by -S- is interrupted, for example, by -O- from one to five times, e.g. from one to three times or once or twice, resulting in, for example, structural units such as $-S(CH_2)_2OH$, $-O(CH_2)_2OH$, $-O(CH_2)_2OCH_3$, $-O(CH_2CH_2O)_2CH_2CH_3$, $-CH_2$-O-CH_3, $-CH_2CH_2$-O-CH_2CH_3, $-[CH_2CH_2O]_y-CH_3$ wherein y = from 1 to 5, $-(CH_2CH_2O)_5CH_2CH_3$, $-CH_2-CH(CH_3)-O-CH_2-CH_2CH_3$ and $-CH_2-CH(CH_3)-O-CH_2-CH_3$.

C_3-C_{12}Cycloalkyl is, for example, cyclopropyl, cyclopentyl, cyclohexyl, cyclooctyl or cyclododecyl. C_5-C_{12}Cycloalkyl is, for example, cyclopentyl, cyclohexyl, cyclooctyl or cyclododecyl. Preference is given to cyclopentyl and cyclohexyl, especially cyclohexyl.

C_1-C_{18}Alkoxy is e.g. methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy or tert-butoxy, pentyloxy, hexyloxy, heptyloxy, decyloxy or dodecyloxy, for example C_1-C_{12}alkoxy, C_1-C_8alkoxy, preferably C_1-C_4alkoxy, especially methoxy.
C_1-C_8Alkoxy is as defined hereinbefore up to the appropriate number of carbon atoms.

C_1-C_{12}Alkythio is linear or branched and is e.g. methylthio, ethylthio, n-propylthio, isopropylthio, n-butylthio, isobutylthio, sec-butylthio or tert-butylthio, pentylthio, hexylthio, heptylthio, decylthio or dodecylthio, for example C_1-C_8alkylthio, preferably C_1-C_4alkylthio, especially methylthio.

An O- or S-containing, 5- or 6-membered heterocyclic ring is, for example, furyl, thienyl, oxinyl or dioxinyl.

An O-, S- or N-containing, 5- or 6-membered heterocyclic ring is, for example, furyl, thienyl, pyrrolyl, pyridyl, oxinyl or dioxinyl.

C_2-C_{12}Alkenyl is, for example, allyl, methallyl, 1,1-dimethylallyl, butenyl, hexenyl, octenyl or dodecenyl, for example C_2-C_8alkenyl or C_2-C_4alkenyl, especially allyl. C_2-C_4Alkenyl is, for example, allyl, methallyl, 1,1-dimethylallyl or butenyl.

The radical -O(CH_2CH_2O)$_q$-C_1-C_{16}alkyl represents from 1 to 20 consecutive ethylene oxide units, the chain thereof being terminated by a C_1-C_{16}alkyl. q is preferably from 1 to 10, for example from 1 to 8, especially from 1 to 6. The chain of ethylene oxide units is terminated preferably by a C_1-C_{10}alkyl, for example by a C_1-C_8alkyl, especially by a C_1-C_4alkyl.

Phenyl-C_1-C_4alkyl is, for example, benzyl, phenylethyl, α-methylbenzyl or α,α-dimethylbenzyl, especially benzyl.

Substituted phenyl, naphthyl or biphenyl is mono- to penta-, for example, mono- to tetra-, e.g. mono-, di- or tri-, especially di- or tri-substituted.

R_{31}, R_{32} and R_{33} as substituted phenyl, naphthyl or biphenyl are substituted, for example, by linear or branched C_1-C_8alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl,

sec-butyl, tert-butyl, pentyl, hexyl, heptyl or octyl, or by linear or branched C_1-C_8-alkoxy, such as methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy, tert-butoxy, hexyloxy or octyloxy, or by linear or branched C_1-C_8alkylthio, such as methylthio, thylthio, n-propylthio, isopropylthio, n-butylthio, isobutylthio, sec-butylthio, tert-butylthio, pentylthio or hexylthio, or by halogen, such as fluorine, chlorine, bromine or iodine. Preferred substituents of R_{31}, R_{32} and R_{33} as phenyl, naphthyl and biphenyl are C_1-C_4alkyl, especially methyl, C_1-C_4alkoxy, especially methoxy, and chlorine. R_{31}, R_{32} and R_{33} are specially, for example, 2,4,6-trimethylphenyl, 2,6-dichlorophenyl, 2,6-dimethylphenyl or 2,6-dimethoxyphenyl.

Examples of n-valent metals (n = from 1 to 3) are Na, Li, K, Mg, Ca, Ba, Fe, Co and Al.

When R_{31} and R_{32} are C_4-C_7alkylene and, together with the P atom to which they are bonded, form a ring, that ring (including the P atom) is preferably five- or six-membered.

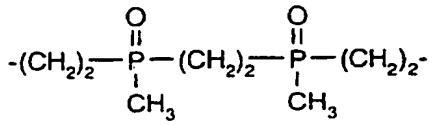
C_1-C_8Alkylphenyl is, for example, C_1-C_4alkylphenyl, for example tolyl, xylyl, mesityl, ethylphenyl or diethylphenyl, preferably tolyl or mesityl.
C_1-C_4Alkylnaphthyl is naphthyl substituted by methyl, ethyl and/or propyl or butyl.

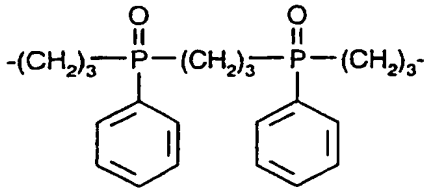
C_1-C_{18}alkylene and C_1-C_{12}alkylene are linear or branched alkylene, for example methylene, ethylene, propylene, isopropylene, n-butylene, sec-butylene, isobutylene, tert-butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, dodecylene, tetradecylene, heptadecylene or octadecylene. X and Y are each especially C_1-C_{12}alkylene, for example ethylene, decylene, $-CH(C_{11}H_{23})-$, $-CH(CH_3)-CH_2-$, $-CH(CH_3)-(CH_2)_2-$, $-CH(CH_3)-(CH_2)_3-$,

$-C(CH_3)_2-CH_2-$ or $-CH_2-\underset{\displaystyle C_2H_5}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-$.

When X is C_2-C_{18}alkylene interrupted by -O-, -S-, $-NR_{35}$-, $-P(O)R_{36}$- or by $-SO_2$-, there are obtained, for example, structural units such as $-CH_2-O-CH_2-$, $-CH_2CH_2-O-CH_2CH_2-$, $-[CH_2CH_2O]_y-$ wherein y = from 1 to 9, $-(CH_2CH_2O)_7CH_2CH_2-$, $-CH_2-CH(CH_3)-O-CH_2-CH(CH_3)-$, $-CH_2-S-CH_2-$, $-CH_2CH_2-S-CH_2CH_2-$, $-CH_2CH_2CH_2-S-CH_2CH_2CH_2-$, $-(CH_2)_3-S-(CH_2)_3-S-(CH_2)_3-$, $-CH_2-(NR_{35})-CH_2-$,

$-CH_2CH_2-(NR_{35})-CH_2CH_2-$, $-CH_2-(P(O)R_{36})-CH_2-$, $-CH_2CH_2-(P(O)R_{36})-CH_2CH_2-$,





, $-CH_2-SO_2-CH_2-$ and

$-CH_2CH_2-SO_2-CH_2CH_2-$.

C_1-C_4Alkoxy substituents are, for example, methoxy, ethoxy, propoxy and butoxy, especially methoxy. C_1-C_6alkylene substituted by C_1-C_4alkoxy or by $-COOR_{37}$ is, for example, $-CH(OCH_3)-$ or $-CH(COOCH_3)-CH_2-$.

C_1-C_4Alkylphenyl is, for example, tolyl, xylyl, mesityl, ethylphenyl or diethylphenyl, preferably tolyl or mesityl.

C_1-C_4Alkylnaphthyl is naphthyl substituted by methyl, ethyl and/or propyl or butyl.

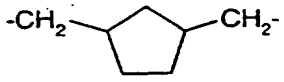
Phenyl-C_1-C_4alkyl is, for example, benzyl, phenylethyl, α-methylbenzyl or α,α-dimethylbenzyl, especially benzyl.

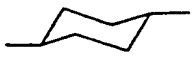
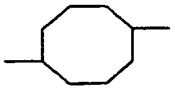
Naphthyl-C_1-C_4alkyl is, for example, naphthylmethyl, naphthylethyl, naphthyl-(1-methyl)-eth-1-yl or naphthyl-(1,1-dimethyl)eth-1-yl, especially naphthylmethyl.

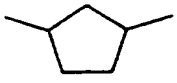
Phenyl-C_1-C_4alkoxy is to be understood as being, for example, benzyloxy, phenylethyloxy, α-methylbenzyloxy or α,α-dimethylbenzyloxy, especially benzyloxy.

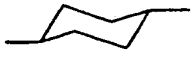
Naphthyl-C_1-C_4alkoxy is, for example, naphthylmethyloxy or naphthylethyloxy.

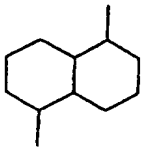
Examples of groups of formula (A_1) wherein the sum of d and f is from 3 to 8 are:

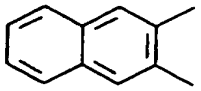
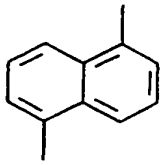
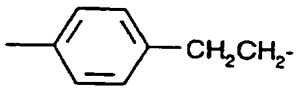
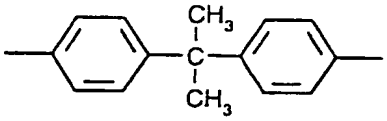
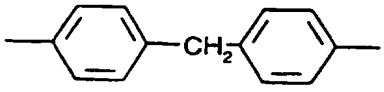
d+f = 3  ,  , d+f=4  ,

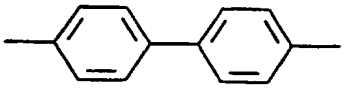
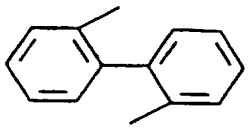
 and d+f = 6  .

Preference is given to  ,  and

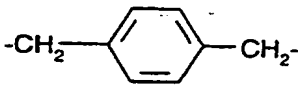
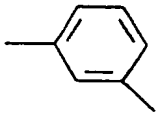
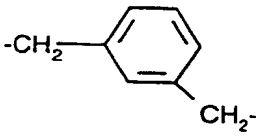
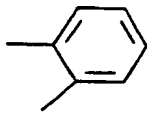
 .

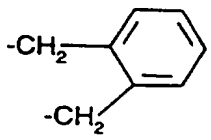
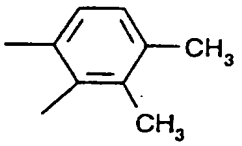
Examples of groups of formulae A_2, A_3, A_4, A_5, A_6, A_7, A_8 and A_9 are  ,

 ,  and  . Examples of groups of formula A_{10} are  ,  ,

 and  .

Examples of unsubstituted and substituted phenylene and xylylene are  ,

 ,  ,  ,  ,

 and  .

The preparation of compounds of formulae I and Ia is generally known and some of the compounds are available commercially. The preparation of oligomeric compounds of formula I is described, for example, in EP-A-161 463. A description of the preparation of compounds of formula Ia may be found, for example, in EP-A-209 831.

The preparation of compounds of formula Ib is described, for example, in EP-A-284 561. The compounds of formula III are prepared, for example, in the manner disclosed in EP-A-184 095.
Some compounds of formulae Ib, II and III are also available commercially.

Preference is given to compounds of formula I wherein R_1 is hydrogen, C_1-C_{12}alkyl or -OCH_2CH_2-OR_5; R_2 and R_3 are each independently of the other C_1-C_6alkyl, phenyl or C_1-C_{16}alkoxy or R_2 and R_3, together with the carbon atom to which they are bonded, form a cyclohexyl ring; R_4 is hydroxy or C_1-C_{16}alkoxy; R_5 is hydrogen or $-\overset{O}{\overset{\|}{C}}-CH=CH_2$;

and to compounds of formula (Ia) wherein R_9, R_{10}, R_{11} and R_{12} are hydrogen;
and to compounds of formula (Ib) wherein R_{13} is hydrogen; R_{14} is C_1-C_4alkylthio or $N(R_{17}R_{18})$; R_{15} is C_1-C_8alkyl; R_{16} is phenyl; R_{17} and R_{18} are each independently of the other C_1-C_4alkyl or R_{17} and R_{18}, together with the nitrogen atom to which they are bonded, form a saturated six-membered ring, which may be interrupted by -O-;
and to compounds of formula II wherein R_{21} is phenyl and R_{22} is C_1-C_{12}alkyl;
and to compounds of formula III wherein Z is O; R_{31} and R_{32} are each independently of the other C_1-C_{18}alkyl; phenyl that is unsubstituted or mono- to penta-substituted by C_1-C_8alkyl and/or by C_1-C_8-alkoxy; or a group COR_{33}; and R_{33} is phenyl that is unsubstituted or mono- to tetra-substituted by C_1-C_8alkyl or by C_1-C_8alkoxy.

Preferably, R_2 and R_3 in formula I are each independently of the other C_1-C_6alkyl or, together with the carbon atom to which they are bonded, form a cyclohexyl ring, and R_4 is hydroxy.

More especially, R_2 and R_3 in formula I are identical and are each methyl, and R_4 is hydroxy or isopropoxy.

In formula Ia R_9-R_{12} are preferably hydrogen.

Preferably, R_{16} in formula Ib is phenyl or -$CH=CHR_{20}$, R_{14} is C_1-C_4alkylthio or $N(R_{17})_2$, and R_{15}, R_{17} and R_{18} are C_1-C_4alkyl.

In formula II R_{21} is preferably phenyl and R_{22} is C_1-C_4alkyl.

Preferably, R_{31} in formula III is COR_{33} wherein R_{33} is phenyl mono- to tetra-substituted by C_1-C_4alkyl, C_1-C_4alkoxy and/or by halogen, and R_{32} is C_1-C_{12}alkyl, unsubstituted phenyl or phenyl mono- to penta-substituted by C_1-C_4alkyl and/or by C_1-C_4alkoxy.

Furthermore, in formula III preferably R_{31} and R_{32} are phenyl and R_{33} is phenyl mono- to tri-substituted by C_1-C_4alkyl and/or by C_1-C_4alkoxy.

Z is preferably O.

As component (C) special preference is given to 1-hydroxy-cyclohexyl-phenyl ketone, 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one or 2-hydroxy-2-methyl-1-phenyl-propanone, (4-morpholino-benzoyl)-1-benzyl-1-dimethylamino-propane or (4-methylthiobenzoyl)-1-methyl-1-morpholino-ethane, 2,2-dimethoxy-1,2-diphenylethan-1-one, 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide, bis(2,6-dimethoxybenzoyl-2,4,4-trimethylpentyl-phosphine oxide, bis(2,4,6-trimethylbenzoyl)-(2-methylprop-1-yl)-phosphine oxide, bis(2,4,6-trimethylbenzoyl)-phenyl-phosphine oxide, and mixtures of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphine oxide with 1-hydroxy-cyclohexyl-phenyl ketone, hydroxy-2-methyl-1-phenyl-propanone or 2-methoxy-1-phenyl-ethane-1,2-dione; or of bis(2,4,6-trimethylbenzoyl)-phenyl-phosphine oxide with 1-hydroxy-cyclohexyl-phenyl ketone, hydroxy-2-methyl-1-phenyl-propanone or 2-methoxy-1-phenyl-ethane-1,2-dione; or of 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide with 1-hydroxy-cyclohexyl-phenyl ketone, hydroxy-2-methyl-1-phenyl-propanone or 2-methoxy-1-phenyl-ethane-1,2-dione.

The photopolymerisable compositions contain the photoinitiator (C) advantageously in an amount from 0.05 to 20 % by weight, preferably from 2 to 10 % by weight, based on 100 parts of component (A).

When the photoinitiator (C) is a mixture of a compound of formula I, Ia, Ib or II with a compound of formula III, the proportion of the compound(s) of formula I, Ia, Ib or II in the mixture is, for example, from 25 to 90 %, e.g. from 25 to 75 %, preferably from 50 to 75 %.

Preference is given to a composition comprising (A) polyester polyol, acrylate polyol or hexamethoxymethylmelamine and (B) isocyanurate or OH-functionalised acrylate and (C) 1-hydroxy-cyclohexyl-phenyl ketone or 25 % bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphine oxide and 75 % 1-hydroxy-cyclohexyl-phenyl ketone or 4-[(2-hydroxyethoxy)-benzoyl]-1-hydroxy-1-methyl-ethane.

It is characteristic of the composition that it comprises an OH-, NH_2-, COOH-, epoxy- or NCO-functionalised component that also, in addition, contains free double bonds separated from the functional group by a spacer group of at least 4 linearly linked atoms (B), and a photoinitiator (C). In accordance with the process according to the invention, the addition of those components allows a further cross-linking of the surface coating on irradiation with light after the thermal curing, resulting in a surface coating having improved surface properties, especially in respect of the hardness and resistance to scratching.

The surface coatings according to the invention may comprise an organic solvent or solvent mixture in which the binder and/or the cross-linker is (are) soluble or dispersible. The composition may, however, also be an aqueous solution or dispersion. It is also possible, for example, for one of the two components to serve as the dispersion medium or dissolution medium for the other component. The vehicle may also be a mixture of an organic solvent and water. The coating may also be a high-solids surface coating or may be solvent-free (for example, powder coating composition).

The compositions according to the invention are prepared by mixing all the components. It is also possible, for example, first to link only the OH-, NH_2-, COOH-, epoxy- or NCO-functionalised component (B) with component (A), or with a constituent thereof, *via* the functional group in question, and thereafter to mix in all the other constituents.

The compositions according to the invention may be applied to any desired substrates, for example to metal, wood, plastics or ceramic materials. They are preferably used as finishing lacquers for the surface-coating of motor vehicles. When the finishing lacquer consists of two layers the lower layer of which is pigmented and the upper layer of which is not pigmented, the coating according to the invention may be used for the upper or the lower layer or for both layers, but preferably for the upper layer.

The compositions according to the invention may be applied to the substrates in accordance with the customary procedures, for example by painting, spraying, pouring, immersion or electrophoresis; see also Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A18, pp. 491-500.

The invention therefore relates also to a process for the coating of a substrate wherein a composition according to the invention is applied to the surface of the substrate, cured by means of heating and then irradiated with UV light.

In addition to the photoinitiator the compositions may comprise further customary additives, or it is possible to add further additives to the formulation in the process according to the invention.
For example, the composition may comprise further components in addition to components (A), (B) and (C), or in the process according to the invention it is possible to add to components (B) and (C) further additives, for example light stabilisers, solvents, pigments, dyes, plasticisers, stabilisers, thixotropic agents, drying catalysts and/or flow improvers. Possible components are, for example, such as are described in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A18, pp. 429-471, VCH, Weinheim 1991.

UV-absorbers, for example those of the hydroxyphenyl-benzotriazole, hydroxyphenyl-benzophenone, oxalic acid amide or hydroxyphenyl-s-triazine type, may be added as light stabilisers. There may be used, for example, individual compounds or mixtures of those compounds with or without the use of sterically hindered amines (HALS).

Possible drying catalysts, or curing catalysts, are, for example, organic metal compounds, amines, amino-group-containing resins and/or phosphines. Organic metal compounds are, for example, metal carboxylates, especially those of the metals Pb, Mn, Co, Zn, Zr and Cu, and metal chelates, especially those of the metals Al, Ti and Zr, and organometal compounds, for example organotin compounds.
Examples of metal carboxylates are the stearates of Pb, Mn and Zn, the octanoates of Co, Zn and Cu, the naphthenates of Mn and Co and the corresponding linoleates, resinates and tallates.

Examples of metal chelates are the aluminium, titanium and zirconium chelates of acetylacetone, ethyl acetoacetate, salicylaldehyde, salicylaldoxime, o-hydroxyacetophenone and ethyltrifluoroacetoacetate and the alcoholates of those metals.
Examples of organotin compounds are dibutyltin oxide, dibutyltin dilaurate and dibutyltin dioctanoate.
Examples of amines are especially tertiary amines, for example tributylamine, triethanolamine, N-methyl-diethanolamine, N-dimethylethanolamine, N-ethylmorpholine, N-methylmorpholine and diazabicyclooctane (triethylenediamine) and salts thereof. Further examples are quaternary ammonium salts, for example trimethylbenzylammonium chloride.
Amino-group-containing resins act simultaneously as binder and curing catalyst. Amino-group-containing acrylate copolymers are examples thereof.
As curing catalyst there may also be used phosphines, for example triphenyl-phosphine.
The pigments may be inorganic, organic or metallic pigments. Preferably, the coatings according to the invention contain no pigments and are used as clear lacquer.

Preference is given to the use of the composition according to the invention as a coating, especially as a finishing lacquer for use in the furniture industry and automobile industry, more especially as a pigmented or non-pigmented top layer of the surface coating. The use thereof for underlying layers is, however, also possible.
When the composition according to the invention is used in the underlying layer, with the simultaneous use of a UV-curable finishing lacquer, the adhesion of the UV-curable finishing lacquer to the underlying layer is improved as a result of the reaction of the double bonds present in each of the layers.

Preference is given to non-pigmented compositions and to a curing process without the addition of pigments.

The curing of the compositions according to the invention is carried out thermally at first. The surface is after-cured by subsequent irradiation with UV light.
Accordingly, in the curing process according to the invention, the coating to be cross-linked is first of all cured by the action of heat and the surface hardness is improved by the subsequent irradiation with UV light.

The thermal curing is carried out generally in an oven, for example a circulating-air oven, or by means of irradiation with IR lamps. Curing at room temperature without aids is likewise possible, depending on the binder system used. The curing temperatures are generally from room temperature to 150°C, for example from 25 to 150°C or from 50 to 150°C. In the case of powder coating compositions, the curing temperatures may be even higher, for example up to 250°C.

The photochemical curing step is carried out usually using light of wavelengths from about 200 nm to about 600 nm, especially from 200 to 450 nm. As light sources there are used a large number of the most varied types. Both point sources and planiform projectors (lamp carpets) are suitable. Examples are: carbon arc lamps, xenon arc lamps, medium-, high- and low-pressure mercury lamps, optionally doped with metal halides (metal halide lamps), microwave-excited metal-vapour lamps, excimer lamps, superactinic fluorescent tubes, fluorescent lamps, argon filament lamps, electronic flash lamps, photographic flood lights, electron beams and X-rays generated by means of synchrotrons or laser plasma. The distance between the lamp and the substrate according to the invention to be irradiated may vary, for example, from 2 cm to 150 cm, according to the intended use and the type and strength of the lamp. Laser-light sources, for example excimer lasers, are especially suitable. The selection of the type of lamp is dependent especially on the type of photoinitiator (C) used. For example, bisacylphosphine oxide photoinitiators are excited even by lamps having an emission spectrum of relatively long wavelength.

The Examples that follow illustrate the invention further. Unless stated otherwise, parts or percentages relate, as they do in the rest of the description and in the patent claims, to weight.

Examples 1-4:

A 2-component polyurethane clear lacquer is prepared by mixing:

50.10 parts of Desmophen® 680; polyester polyol; 70% in butyl acetate (Bayer AG)

0.48 part of Baysilone® OL 17; flow improver; 10% in xylene (Bayer AG)

1.45 parts of diazabicyclooctane (DABCO); accelerator; 10% in butyl acetate

14.64 parts of xylene/butyl acetate/Solvesso® 100 (2/2/1); (Solvesso® = aromatic hydrocarbons (Esso))

14.76 parts of Desmodur® N 3390; isocyanurate; 90% (Bayer AG)

18.57 parts of xylene/butyl acetate/Solvesso® 100 (2/2/1)

100.00 parts of resin solid

To a sample of the lacquer thus prepared there are added 10%, and to a further sample 15%, (based on the resin solid) Ebecryl® 600, OH-functional acrylate resin (UCB) and 5% photoinitiator (PI-1 or PI-2); the mixture is applied to a white coil-coating sheet, air-dried for 15 minutes and stoved at 80°C for 30 minutes. A dry film thickness of approximately 40 µm is obtained.

10 minutes after the thermal curing, the pendulum hardness according to König (DIN 53157) is determined. Irradiation is then carried out using a UV-processor (2 x 120 W/cm) at a band speed of 10 m/min and the pendulum hardness is determined again. The higher the values of the pendulum hardness measurement, the more durable and harder is the cured surface.

The initiators used and the results of the pendulum hardness measurements can be found in Table 1 below.

Table 1

Example	OH-functional resin	Photo-initiator	Pendulum hardness [sec]		
			before irradiation	after irradiation	increase
1	10 %	PI-1	29	41	12
2	10 %	PI-2	34	47	13
3	15 %	PI-1	31	46	15
4	15 %	PI-2	34	53	19

PI-1: 1-Hydroxy-cyclohexyl-phenyl ketone (Irgacure® 184; Ciba Spezialitätenchemie)

PI-2: 25 % bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphine oxide + 75 % 1-hydroxy-cyclohexyl-phenyl ketone (Irgacure® 1800; Ciba Spezialitätenchemie)

Example 5:

A high-solids clear lacquer is prepared by mixing:

56.16 g of Joncryl® 510; OH-functional acrylate; 80% in xylene (SC Johnson Polymer BV/Holland)

19.18 g of Cymel® 303; hexamethoxymethylmelamine (Cytec Industries/USA)

14.16 g of butanol

9.89 g of methylamyl ketone (MAK)

0.61 g of DC-57; flow improver; 10% in MAK (DOW Corning/Belgium)

100.00 g

0.5 % p-toluenesulfonic acid (10 % in butanol) is added to that mixture.

To a sample of the lacquer thus prepared there are added 15 % 8-hydroxyoctyl acrylate (HOAc) and to another sample 15 % Tegomer® V-Si 2150 (α,ω-acryloxyorgano-functional polydimethylsiloxane, Goldschmidt AG/Germany), and to each of two further samples there are added, in addition, 6 % 4-[(2-hydroxyethoxy)-benzoyl]-1-hydroxy-1-methyl-ethane (Irgacure®2959, Ciba Spezialitätenchemie/Switzerland) which has been dissolved beforehand in methyl ethyl ketone. The samples are each applied to a white coil-coating

sheet, air-dried for 15 minutes and stoved at 120°C for 30 minutes. A dry film thickness of approximately 45 µm is obtained.

After the thermal curing, the sample sheets are cooled to 50°C and irradiated using a UV-processor (2 x 81 W/cm) at a band speed of 5 m/min. The pendulum hardness according to König (DIN 53157) is determined before and after irradiation.

The results of the pendulum hardness measurements are shown in Table 2.

Table 2

Photoinitiator Resin	Pendulum hardness [sec]		Increase
	before irradiation	after irradiation	
Without photoinitiator HOAc	57	64	7
Without photoinitiator Tegomer	59	57	-2
With photoinitiator HOAc	53	95	42
With photoinitiator Tegomer	95	113	18

A clear increase in the pendulum hardness is observed in the case of the samples to which photoinitiator has been added.

Example 6:

A high-solids clear lacquer is prepared by mixing:

53.4 g of Joncryl® 510; OH-functional acrylate; 80 % in xylene (SC Johnson Polymer BV/Holland)

19.18 g of Cymel® 303; hexamethoxymethylmelamine (Cytec Industries/USA)

14.16 g of butanol

12.65 g of methylamyl ketone (MAK)

0.61 g of DC-57; flow improver; 10 % in MAK (DOW Corning/Belgium)

100.00 g

0.5 % p-toluenesulfonic acid (10 % in butanol) is added to that mixture.
To a sample of the lacquer thus prepared there are added 15 % 8-hydroxyoctyl acrylate (HOAc) and to another sample 15 % Tegomer® V-Si 2150 (α,ω-acryloxyorgano-functional polydimethylsiloxane, Goldschmidt AG/Germany), and to each of two further samples there are added, in addition, 6 % 4-[(2-hydroxyethoxy)-benzoyl]-1-hydroxy-1-methyl-ethane (Irgacure® 2959, Ciba Spezialitätenchemie/Switzerland) which has been dissolved beforehand in methyl ethyl ketone. The samples are each applied to a white coil-coating sheet, air-dried for 15 minutes and stoved at 120°C for 30 minutes. A dry film thickness of approximately 45 µm is obtained.
After the thermal curing, the sample sheets are cooled to 50°C and irradiated using a UV-processor (2 x 81 W/cm) at a band speed of 5 m/min. The pendulum hardness according to König (DIN 53157) is determined before and after irradiation. The results of the pendulum hardness measurements are listed in Table 3.

Table 3

Photoinitiator Resin	Pendulum hardness [sec]		Increase
	before irradiation	after irradiation	
Without photoinitiator HOAc	53	57	4
Without photoinitiator Tegomer	69	80	11
With photoinitiator HOAc	69	102	43
With photoinitiator Tegomer	63	95	32

Example 7:

To a sample of a 2C polyurethane lacquer mixture, as described in Example 1, there are added 15 % 8-hydroxyoctyl acrylate (HOAc) and to another sample 15 % 4-hydroxybutyl acrylate (HBAc), and to each of two further samples there are added, in addition, 6 % 4-[(2-

hydroxyethoxy)-benzoyl]-1-hydroxy-1-methyl-ethane (Irgacure® 2959, Ciba Spezialitäten-chemie/Switzerland) which has been dissolved beforehand in methyl ethyl ketone. The samples are each applied to a white coil-coating sheet, air-dried for 15 minutes and stoved at 80°C for 30 minutes. A dry film thickness of approximately 45 µm is obtained.

After the thermal curing, the sample sheets are cooled to 50°C and irradiated using a UV-processor (2 x 81 W/cm) at a band speed of 5 m/min. The MEK-resistance is determined before and after irradiation. For that purpose, a piece of felt soaked with methyl ethyl ketone is laid on the lacquer surface and covered with a watch glass; the time until blister formation is measured. The longer the time period until blister formation, the more resistant is the surface-coating formulation. The results can be found in Table 4.

Table 4

Photoinitiator Resin	MEK-resistance [min]		Increase
	before irradiation	after irradiation	
Without photoinitiator HOAc	2	2	0
Without photoinitiator HBAc	2	2	0
With photoinitiator HOAc	2	25	23
With photoinitiator HBAc	2	15	13

The improvement in the resistance to solvent when a photoinitiator has been added for the subsequent irradiation is clearly discernible.

Example 8:

A 2C polyurethane lacquer is prepared by mixing:

54.80 g of Macrynal® SM 510N; acrylate polyol (Hoechst/Germany)
0.15 g of Byk® 300; flow improver (Byk-Chemie/Germany)
0.07 g of Nuodex zinc octanoate; accelerator
11.50 g of butyl glycol acetate
4.70 g of Solvesso 100; aromatic hydrocarbons (Esso)
5.68 g of methyl isobutyl ketone (MIBK)
23.10 g of Desmodur® N75; isocyanate (Bayer AG/Germany)

100.00 g

To a sample of the lacquer thus prepared there are added 15% 8-hydroxyoctyl acrylate (HOAc) and to a further sample there are added, in addition, 6% 4-[(2-hydroxyethoxy)-benzoyl]-1-hydroxy-1-methyl-ethane (Irgacure® 2959, Ciba Spezialitätenchemie/Switzerland) which has been dissolved beforehand in methyl ethyl ketone. The samples are each applied to a white coil-coating sheet, air-dried for 15 minutes and stoved at 130°C for 30 minutes. A dry film thickness of approximately 45 µm is obtained.

After the thermal curing, the sample sheets are cooled to 50°C and irradiated using a UV-processor (2 x 81 W/cm) at a band speed of 5 m/min. The pendulum hardness according to König (DIN 53157) is determined before and after irradiation. The results of the pendulum hardness measurements are reproduced in Table 5.

Table 5

Photoinitiator Resin	Pendulum hardness [sec]		Increase
	before irradiation	after irradiation	
Without photoinitiator HOAc	118	120	2
With photoinitiator HOAc	120	140	20

What is claimed is:

1. A process for the curing of a polymerisable composition comprising

(A) a coating system based on

(I) a polyacrylate polyol and/or polyester polyol with melamine or

(II) a polyacrylate polyol and/or polyester polyol with a blocked or unblocked polyisocyanate or

(III) a carboxyl-, anhydride- or amino-functional polyester and/or polyacrylate with an epoxy-functional polyester or polyacrylate, or

(IV) a mixture of (I), (II), (III) and/or (IV),

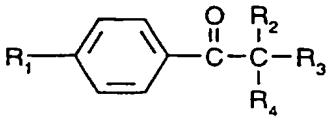
(B) an OH-, NH_2-, COOH-, epoxy- or NCO-functional resin containing, in addition, at least one ethylenically unsaturated double bond, it being necessary for a spacer group of at least 4 linearly linked atoms to be present between the double bond and the functional group,

wherein components (A) and (B) do not contain halogen, and

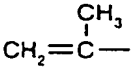
(C) at least one photoinitiator,

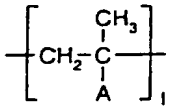
by thermal treatment and, for the purpose of improving the surface properties, subsequent photochemical treatment with light of a wavelength from 200 to 600 nm.

2. A process according to claim 1 wherein in the composition the photoinitiator (C) is a compound of formula I

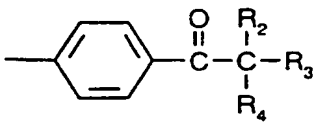


(I) wherein

R_1 is hydrogen, C_1-C_{18}alkyl, C_1-C_{18}alkoxy, -OCH_2CH_2-OR_5, a group 

or a group  wherein

l is an integer from 2 to 10 and

A is a radical  ;

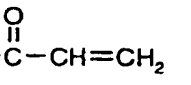
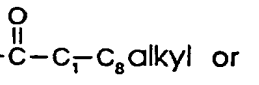
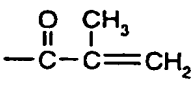
R_2 and R_3 are each independently of the other hydrogen, C_1-C_6alkyl, phenyl, C_1-C_{16}alkoxy, $OSiR_6R_7R_8$ or $-O(CH_2CH_2O)_q$-C_1-C_{16}alkyl wherein

q is an integer from 1 to 20, or

R_2 and R_3, together with the carbon atom to which they are bonded, form a cyclohexyl ring;

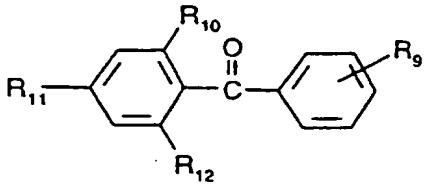
R_4 is hydroxy, C_1-C_{16}alkoxy or $-O(CH_2CH_2O)_q$-C_1-C_{16}alkyl;

with the proviso that R_2, R_3 and R_4 are not all simultaneously C_1-C_{16}alkoxy or $-O(CH_2CH_2O)_q$-C_1-C_{16}alkyl;

R_5 is hydrogen, C_1-C_8alkyl,  ,  or  ;

R_6, R_7 and R_8 are each independently of the others C_1-C_4alkyl or phenyl;

or a compound of formula (Ia)

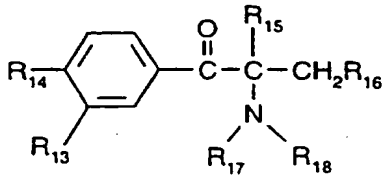


(Ia) wherein

R_9, R_{10}, R_{11} and R_{12} are each independently of the others hydrogen, methyl, phenyl, methoxy, -COOH, unsubstituted or C_1-C_4alkyl-substituted phenyl, or a group $-OCH_2CH_2OR_5$ or $-SCH_2CH_2OR_5$ wherein

R_5 is as defined for formula I;

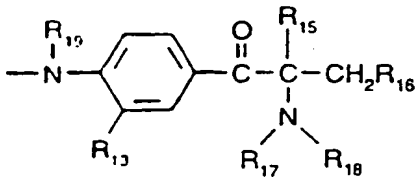
or a compound of formula (Ib)



(Ib) wherein

R_{13} is hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4alkylthio, halogen or a group $N(R_{17}R_{18})$;

R_{14} has one of the meanings indicated for R_{13} or is the group



, in which case the radical R_{13} from formula Ib and the radical R_{13} from this group are together a direct bond and the other radicals are as defined below;

R_{15} is C_1-C_8alkyl;

R_{16} is hydrogen, -CH=CHR_{20}, or phenyl that is unsubstituted or mono- to tri-substituted by C_1-C_{12}alkyl, C_1-C_4alkoxy or by halogen; or

R_{15} and R_{16}, together with the carbon atom to which they are bonded, form a cyclohexyl ring;

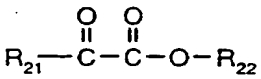
R_{17} and R_{18} are each independently of the other C_1-C_4alkyl or

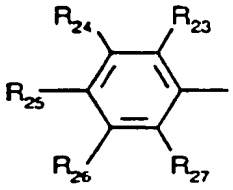
R_{17} and R_{18}, together with the nitrogen atom to which they are bonded, form a five- or six-membered, saturated or unsaturated ring, which may be interrupted by -O-, -NH- or by -N(CH_3)-,

R_{19} is hydrogen or C_1-C_{12}alkyl; and

R_{20} is hydrogen or C_1-C_4alkyl;

or a compound of formula II

 (II) wherein

R_{21} is naphthyl, anthracyl, an O- or S-containing, 5- or 6-membered heterocyclic ring or a group  ;

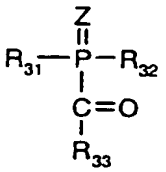
R_{22} is C_1-C_{12}alkyl, cyclohexyl, cyclopentyl, C_2-C_{12}alkenyl, phenyl-C_1-C_4alkyl; phenyl, biphenyl or naphthyl each of which is unsubstituted or mono- to tetra-substituted by C_1-C_4alkyl and/or by C_1-C_4alkoxy; C_2-C_{18}alkyl interrupted one or more times by -O-; or Si(R_{28})(R_{29})(R_{30});

R_{23}, R_{24}, R_{25}, R_{26} and R_{27} are each independently of the others hydrogen, C_1-C_8alkyl,

C_1-C_8alkoxy, C_1-C_8alkylthio, phenyloxy, phenylthio, phenyl that is unsubstituted or mono- to tetra-substituted by C_1-C_4alkyl and/or by C_1-C_4alkoxy, phenyl-C_1-C_4alkyl, halogen or NO_2;

R_{28}, R_{29} and R_{30} are each independently of the others C_1-C_8alkyl, cyclohexyl, cyclopentyl, phenyl or C_1-C_8alkoxy;

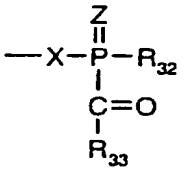
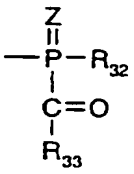
or a compound of formula III



(III) wherein

Z is S or O;

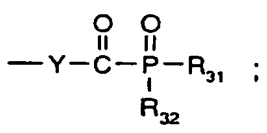
R_{31} and R_{32} are each independently of the other C_1-C_{18}alkyl, C_2-C_{18}alkyl interrupted one or more times by -O-, phenyl-substituted C_1-C_4alkyl, C_2-C_4alkenyl; phenyl, naphthyl or biphenyl each of which is unsubstituted or mono- to penta-substituted by halogen, hydroxy, C_1-C_8alkyl and/or by C_1-C_8alkoxy; C_5-C_{12}cycloalkyl, an O-, S- or N-containing, 5- or 6-membered heterocyclic ring, or a group COR_{33}, or

R_{31} is a radical  ,  , OH, OR_{34}, $O^-NH_4^+$ or $O^-[M^{n+}]_{1/n}$ wherein

n is an integer from 1 to 3 and

M is an n-valent metal ion, or

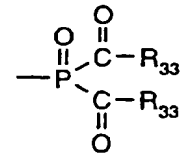
R_{31} and R_{32} together are C_4-C_7alkylene and form a ring together with the P atom to which they are bonded;

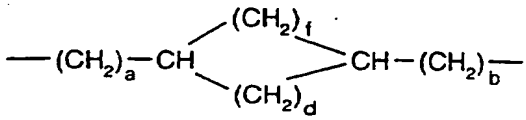
R_{33} is C_1-C_{18}alkyl, C_3-C_{12}cycloalkyl, C_2-C_{18}alkenyl; phenyl, naphthyl or biphenyl each of which is unsubstituted or mono- to tetra-substituted by C_1-C_8alkyl, C_1-C_8alkoxy, C_1-C_8alkylthio and/or by halogen; an O-, S- or N-containing 5- or 6-membered heterocyclic ring, or a group  ;

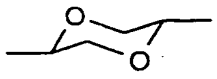
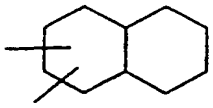
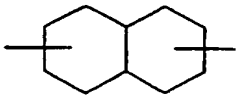
R_{34} is C_1-C_8alkyl, phenyl, naphthyl, C_1-C_8alkylphenyl or C_1-C_4alkylnaphthyl;

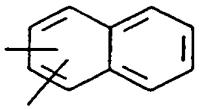
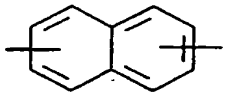
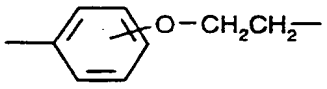
Y is phenylene, C_1-C_{12}alkylene or C_5-C_6cycloalkylene;

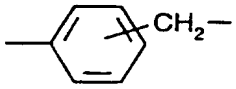
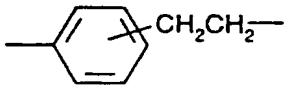
X is C_1-C_{18}alkylene, C_2-C_{18}alkylene interrupted one or more times by -O-, -S-, -NR_{35}-, P(O)R_{36}- or by -SO_2-, or C_1-C_6alkylene substituted by Cl, F, C_1-C_4alkoxy, $COOR_{37}$, phenyl, phenyl-C_1-C_4alkyl, naphthyl-C_1-C_4alkyl, C_1-C_4alkylphenyl, C_1-C_4alkylnaphthyl, phenyl-C_1-C_4alkoxy, naphthyl-C_1-C_4alkoxy and/or by CN, or

X is C_1-C_8alkylene substituted by one or two radicals of formula A  (A), or

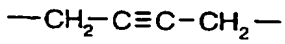
X is a group of formula A_1-A_9  (A_1),

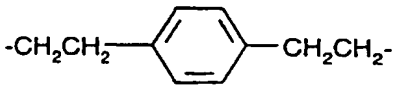
 (A_2),  (A_3),  (A_4),

 (A_5),  (A_6),  (A_7),

 (A_8),  (A_9) wherein

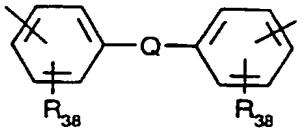
a and **b** are each independently of the other 0 or 1, and the sum of **d** and **f** is an integer from 3 to 8, with the proviso that neither d nor f is 0, or

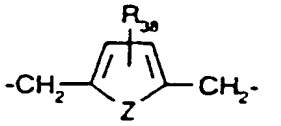
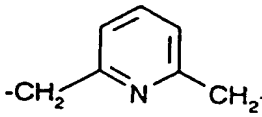
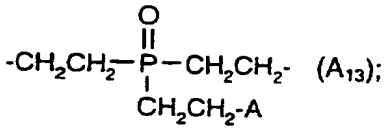
X is a group -CH_2-CH=CH-CH_2- or  , or

X is phenylene, xylylene  or

 each of which is ununsubstituted or mono- to tri-substituted by Cl, F, C_1-C_4alkyl and/or by C_1-C_4alkoxy, or

X is phenylene that is substituted by one or two groups (A) and that, in addition, may be mono- to tri-substituted by Cl, F, C_1-C_4alkyl and/or by C_1-C_4alkoxy, or

X is a group of formula A_{10}-A_{13}  (A_{10}),

 (A_{11}),  (A_{12}),  (A_{13});

Q is a single bond, $CR_{39}R_{40}$, -O-, -S-, $-NR_{35}$-, $-SO_2$-, $-(CH_2)_p$- or -CH=CH-;

p is an integer from 2 to 12;

Z is O or S;

R_{35} is hydrogen, C_1-C_{12}alkyl or phenyl;

R_{36} is C_1-C_4alkyl or phenyl; and

R_{37} is C_1-C_{12}alkyl, C_2-C_{18}alkyl interrupted one or more times by -O-, benzyl, phenyl, cyclopentyl or cyclohexyl;

R_{38} is hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy or halogen;

R_{39} is hydrogen, methyl or ethyl; and

R_{40} is hydrogen or C_1-C_4alkyl;

or a mixture of a compound of formula I, Ia, Ib or II with a compound of formula III.

3. A process according to claim 1 wherein in the composition in formula I

R_1 is hydrogen, C_1-C_{12}alkyl or $-OCH_2CH_2-OR_5$; R_2 and R_3 are each independently of the other C_1-C_6alkyl, phenyl or C_1-C_{16}alkoxy or R_2 and R_3, together with the carbon atom to which they are bonded, form a cyclohexyl ring;

R_4 is hydroxy or C_1-C_{16}alkoxy; R_5 is hydrogen or $-\overset{O}{\overset{\|}{C}}-CH=CH_2$;

and wherein in formula (Ia) R_9, R_{10}, R_{11} and R_{12} are hydrogen;

and in formula (Ib)

R_{13} is hydrogen; R_{14} is C_1-C_4alkylthio or $N(R_{17}R_{18})$; R_{15} is C_1-C_8alkyl;

R_{16} is phenyl; R_{17} and R_{18} are each independently of the other C_1-C_4alkyl or

R_{17} and R_{18}, together with the nitrogen atom to which they are bonded, form a saturated six-membered ring, which may be interrupted by -O-;

wherein in formula II

R_{21} is phenyl and R_{22} is C_1-C_{12}alkyl;
and wherein in formula III
Z is O; R_{31} and R_{32} are each independently of the other C_1-C_{18}alkyl, phenyl that is unsubstituted or mono- to penta-substituted by C_1-C_8alkyl and/or by C_1-C_8alkoxy, or a group COR_{33}; and R_{33} is phenyl that is unsubstituted or mono- to tetra-substituted by C_1-C_8alkyl or by C_1-C_8alkoxy.

4. A process according to claim 1, wherein in the composition the photoinitiator (C) is 1-hydroxy-cyclohexyl-phenyl ketone, 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one or 2-hydroxy-2-methyl-1-phenyl-propanone, (4-morpholino-benzoyl)-1-benzyl-1-dimethylamino-propane or (4-methylthiobenzoyl)-1-methyl-1-morpholino-ethane, 2,2-dimethoxy-1,2-diphenylethan-1-one, 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphine oxide, bis(2,4,6-trimethyl-benzoyl)-(2-methylprop-1-yl)-phosphine oxide, bis(2,4,6-trimethylbenzoyl)-phenyl-phosphine oxide or a mixture of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphine oxide with 1-hydroxy-cyclohexyl-phenyl ketone, hydroxy-2-methyl-1-phenyl-propanone or 2-methoxy-1-phenyl-ethane-1,2-dione; or of bis(2,4,6-trimethylbenzoyl)-phenyl-phosphine oxide with 1-hydroxy-cyclohexyl-phenyl ketone, hydroxy-2-methyl-1-phenyl-propanone or 2-methoxy-1-phenyl-ethane-1,2-dione; or of 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide with 1-hydroxy-cyclohexyl-phenyl ketone, hydroxy-2-methyl-1-phenyl-propanone or 2-methoxy-1-phenyl-ethane-1,2-dione.

5. A process according to claim 1, wherein a composition comprising (A) polyester polyol, acrylate polyol or hexamethoxymethylmelamine and (B) isocyanurate or OH-functionalised acrylate and (C) 1-hydroxy-cyclohexyl-phenyl ketone or 25 % bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphine oxide and 75 % 1-hydroxy-cyclohexyl-phenyl ketone or 4[(2-hydroxyethoxy)-benzoyl]-1-hydroxy-1-methyl-ethane, is used.

6. A process according to claim 1, wherein the composition contains from 0.05 to 20 %, especially from 2 to 10 %, photoinitiator (C), based on 100 parts of component (A).

7. A process according to claim 1, wherein the composition contains from 1 to 50 %, especially from 5 to 30 %, component (B), based on 100 parts of component (A).

8. A process according to claim 1, wherein the composition is a composition based on acrylate/melamine, 2-component polyurethane, 1-component polyurethane, 2-component epoxy or 1-component epoxy/carboxy.

9. A process according to claim 1, wherein the spacer group in component (B) is a group $-\overset{O}{\overset{\|}{C}}-O-(CH_2)_y-$ wherein $y \geq 2$.

10. A composition comprising

(A) a coating system based on

(I) a polyacrylate polyol and/or polyester polyol with melamine or

(II) a polyacrylate polyol and/or polyester polyol with a blocked or unblocked polyisocyanate or

(III) a carboxyl-, anhydride- or amino-functional polyester and/or polyacrylate with an epoxy-functional polyester or polyacrylate, or

(IV) a mixture of (I), (II), (III) and/or (IV),

(B) an OH-, NH_2-, COOH-, epoxy- or NCO-functional resin containing, in addition, at least one ethylenically unsaturated double bond, it being necessary for a spacer group of at least 4 linearly linked atoms to be present between the double bond and the functional group,

wherein components (A) and (B) do not contain halogen, and

(C) at least one photoinitiator.

11. The use of the composition according to claim 10 as a coating.

12. Use according to claim 11 as a finishing lacquer for furniture and in the automobile industry.

13. A process for the coating of a substrate, wherein a composition according to claim 10 is applied to the surface of the substrate, is thermally cured and is then irradiated with UV light.

INTERNATIONAL SEARCH REPORT

Interna ial Application No
PCT/EP 97/03219

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J3/24 C09D167/00 C09D133/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J C09D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 387 304 A (BERNER GODWIN ET AL) 7 February 1995	1
X	see column 5, line 10 - line 12; claim 18; example 1	10,11

X	PATENT ABSTRACTS OF JAPAN vol. 96, no. 5 & JP 08 015861 A (MITSUBISHI RAYON) see abstract	10

X	DE 26 31 949 A (BAYER AG) 19 January 1978 see page 11, paragraph 3	10
A	see page 16, line 1 - line 20	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 October 1997	19. 11. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Schueler, D

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No
PCT/EP 97/03219

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5387304 A	07-02-95	CA 1338535 A	20-08-96
		DE 58909640 D	09-05-96
		EP 0361351 A	04-04-90
		JP 2127025 A	15-05-90
DE 2631949 A	19-01-78	NONE	